

Recent Advances in the Structural Determination of Endohedral Metallofullerenes

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ABSTRACT: The structural determination of endohedral metallofullerenes has attracted special attention in disclosing the formation mechanism and developing new routes to bulk production. Recent advances in the theoretical and experimental studies are summarized with representative mono- and dimetallofullerenes such as $M@C_{82}$ ($M = \text{Ca, Sc, Y, and La}$), $\text{Sc}_2@C_{84}$, and $\text{La}_2@C_{80}$. © 1998 John Wiley & Sons, Inc. *J Comput Chem* **19**: 232–239, 1998

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Introduction

Endohedral metallofullerenes (endohedrally metal-doped fullerenes) have attracted special interest as promising new molecules for material and catalytic applications, because of the unexpected novel properties of empty fullerenes. Since the first success in the extraction of $\text{La}@C_{82}$ in 1991,¹ dimetallofullerenes, such as $\text{Sc}_2@C_{84}$ and $\text{La}_2@C_{80}$, as well as monometallofullerenes,

such as $M@C_{82}$ ($M = \text{group 3 and most lanthanide metals}$), have been demonstrated to be representative and stable examples (the symbol “@” denotes that metals are located inside C_n).^{2–4} Recent, important progress has been marked by the isolation and purification in macroscopic quantities. This has made it possible to investigate the interesting properties and reactivities, as summarized in recent reviews.^{4,5}

The determination of the cage structures and metal positions is currently of primary interest because it is an important clue in disclosing the formation mechanism and developing new routes to bulk production of endohedral metallofullerenes. It is also of current interest whether metal atoms are rigidly attached to fullerene cages

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or whether they move about freely. In the past year, considerable progress has been made in the study of dimetallofullerenes, whereas cage structure and symmetry are still unknown for many monometallofullerenes.⁶ We summarize recent theoretical and experimental advances in structural determination. In theoretical studies, geometries are optimized at the HF level with the effective core potentials on metals,⁷ whereas energies are calculated with nonlocal hybrid density functional theory at the B3P and B3LYP levels.⁸

Results from Calculations and Experiments

Sc₂@C₈₄

For the C₈₄ fullerene, there are 24 isomers which satisfy the so-called isolated pentagon rule.⁹ These are denoted by 1–24 in Figure 1. ¹³C NMR study has shown that only two isomers, **22** (D₂) and **23** (D_{2d}), are most abundantly produced as a 2:1 mixture.¹⁰ These two isomers are very close in energy and much more stable than the remaining 22 isomers.

An interesting question is in which isomers the two Sc atoms are encapsulated. We have suggested that they are equivalently encapsulated inside isomer **23** along the C₂ axis.¹¹ This endohedral structure has D_{2d} symmetry and its optimized structure (**a1**) is shown in Figure 2.^{12,13} Shinohara and coworkers have recently succeeded in observing a total of 11 distinct ¹³C NMR lines (10 lines of nearly equal intensity and 1 of half-intensity).¹⁴ This agrees perfectly with structure **a1** with 11 nonequivalent carbons [10 (× 8) + 1 (× 4) carbons]. This is the first example of the cage-symmetry determination of endohedral metallofullerenes. In addition, only one single ⁴⁵Sc NMR signal, observed by Miyake et al., confirms that two Sc atoms are equivalent¹⁵; the internal rotation is hindered by a large barrier of ca. 50 kcal/mol.¹¹

The distance between the Sc atoms is greatly elongated to 4.029 Å by ca. 1.4 Å from the distance in the ground state of Sc₂ (X⁵Σ_u[−]),¹⁶ and each Sc is only 2.358 Å apart from the nearest-neighbor carbon. This indicates that two Sc atoms are not encapsulated as a dimer. It is of interest that the calculated Sc—Sc and Sc—C distances agree well with the values of Sc—Sc = 3.9 ± 0.1 Å and Sc—C = 2.4 ± 0.2 Å evaluated very recently from the synchrotron X-ray powder diffraction study.¹⁷ The

long Sc—Sc distance is not surprising because electron transfer from the bonding orbitals of Sc₂ is highly favored in fullerene cages. As a result of the transfer of almost two electrons from each Sc to C₈₄, the electronic structure can be formally described as (Sc²⁺)₂C₈₄^{4−} in the ground singlet state¹¹; this has been also verified by the charge density of +2.2 on Sc obtained from an X-ray powder diffraction study.¹⁷

In contrast to the empty case, encapsulation of two Sc atoms inside the most abundant isomer **22** of C₈₄ was calculated to be 10–12 kcal/mol less stable than that inside **23**.^{4,5,18} More stable endohedral structures were found by placing two Sc atoms inside the considerably unstable cages **10** (C_s) and **7** (C_{2v}).^{5,18} As shown in Figure 2, the optimized structures **a2** and **a3** have C_s and C_{2v} symmetry, and are only 5 kcal/mol less stable and 1–2 kcal/mol more stable than **a1**, respectively.¹⁸

Two additional isomers have recently been isolated from a purified sample of Sc₂@C₈₄.¹⁴ The ¹³C NMR spectrum observed successfully for one of these two isomers shows a total of 46 NMR lines [38 + 8 (half-intensity)].¹⁹ This also agrees completely with structure **a2** with 46 nonequivalent carbons [38 (× 2) + 8 (× 1) carbons]. The observation of two ⁴⁵Sc NMR peaks at 298–363 K confirms that two Sc atoms are nonequivalent.¹⁵ Unfortunately, these NMR studies suggest nothing about the metal positions, because all positions on the C_s plane in **a2** satisfy the observed NMR spectra. The metal positions predicted for **a2** in Figure 2 are expected to be determined in a future X-ray study, as was in the case for **a1**.¹⁷ The HOMO and LUMO levels of **a2** are 0.4 eV higher and 0.5 eV lower than those of **a1**, respectively.¹⁸ This may explain why **a2** is less abundantly isolated because of its higher reactivity.

Shinohara and coworkers have recently suggested that the remaining isomer has C_{2v} symmetry but its structure originates from cage **17** (not **7**), because a total of 24 ¹³C NMR lines could be observed,¹⁹ whereas **a3** has 23 nonequivalent carbons. However, the endohedral structure optimized with **17** is 27–29 kcal/mol less stable than **a3**.¹⁸ In addition, it has an unusually small HOMO–LUMO gap due to the remarkably high-lying HOMO level and is thereby highly unstable toward air and moisture. This conflicts with the fact that the remaining isomer differs little in reactivity from **a2**. One of the 24 lines observed might be ascribed to impurities, although the discrepancy should be dissolved in a future study.

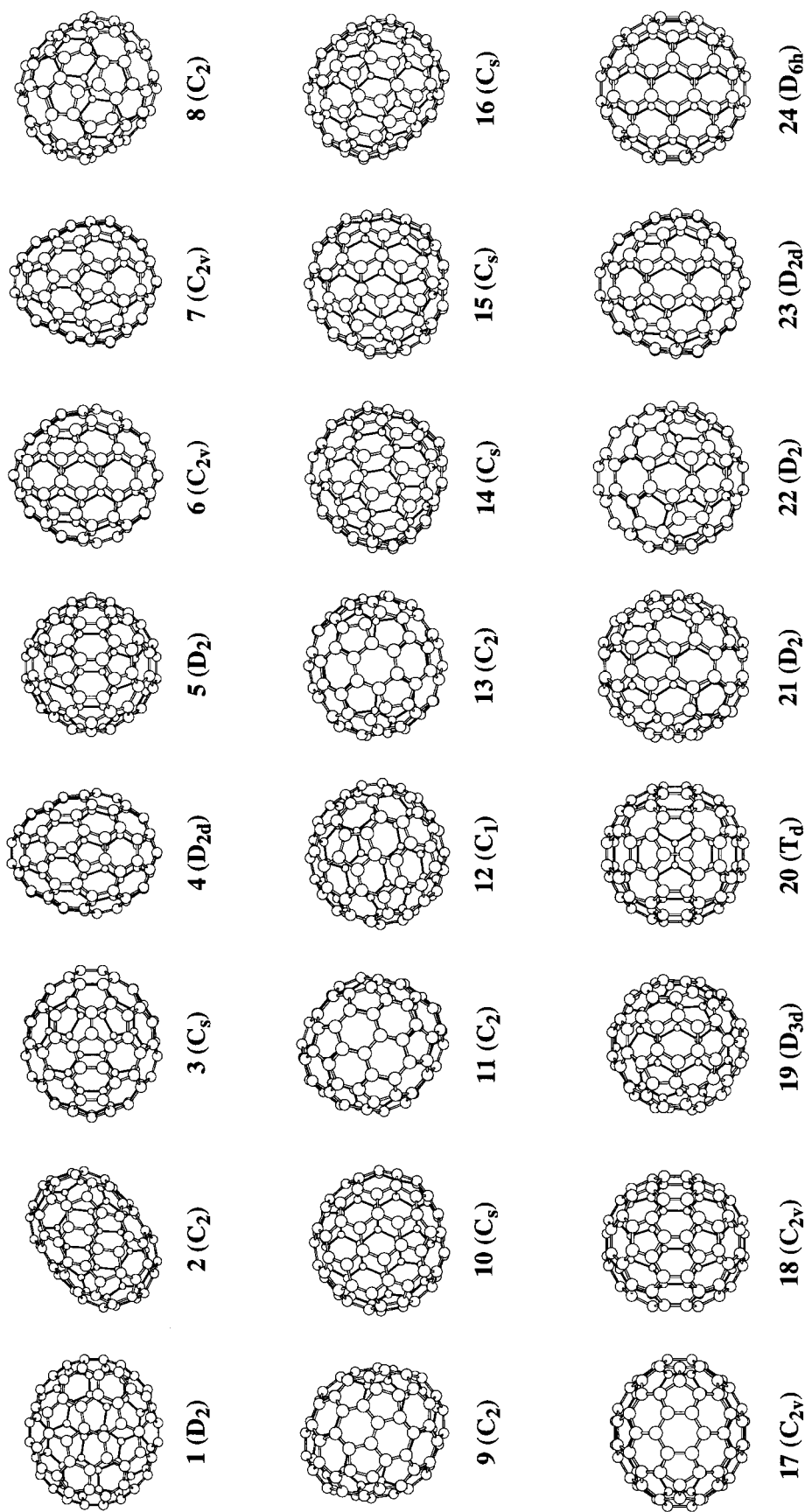


Figure 1. Twenty-four isomers of C_{84} which satisfy the isolated pentagon rule.

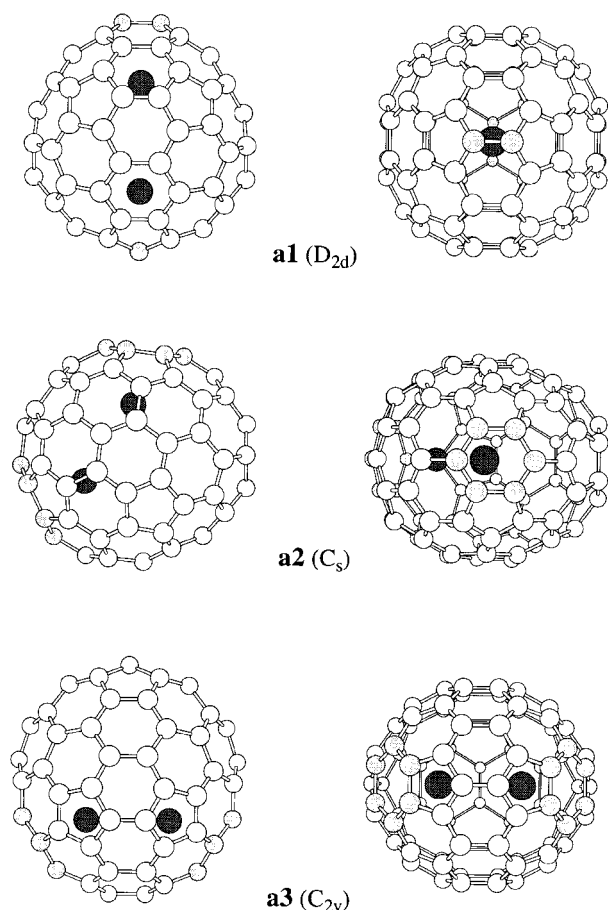


FIGURE 2. Two views of the optimized structures of three isomers of $Sc_2@C_{84}$. The Sc–Sc distances are 4.029 (**a1**), 3.486 (**a2**), and 3.197 (**a3**) Å.

$La_2@C_{80}$

For the C_{80} fullerene, there are seven isomers (D_2 , D_{5d} , C_{2v} , $C_{2v'}$, D_3 , D_{5h} , and I_h) which satisfy the isolated pentagon rule. The D_2 and D_{5d} isomers are close in energy and most stable, whereas the I_h isomer is most unstable; the D_2 and D_{5d} isomers are ca. 52 kcal/mol more stable than I_h .²⁰ The HOMO–LUMO gaps suggest that the D_2 isomer is less reactive (and perhaps more air stable) than D_{5d} .²⁰ Accordingly, the high abundance (> 90%) of the D_2 isomer has recently been verified from a ^{13}C NMR study.²¹

It seems plausible to assume that two La atoms are encapsulated inside the most abundant D_2 or the isoenergetic D_{5d} isomer of C_{80} . From theoretical calculations, however, we have found²⁰ that encapsulation of two La atoms inside the most unstable I_h cage is most favorable; it is 63 and 79 kcal/mol more stable than encapsulation inside the D_2 and D_{5d} cages, respectively. This is because

the I_h cage of C_{80} has only two electrons in the fourfold degenerate HOMOs and can accommodate six more electrons to form a stable closed-shell electronic state of $(La^{3+})_2C_{80}^{6-}$ with a large HOMO–LUMO gap. The most stable endohedral structure (**b1**) optimized with the I_h cage is shown in Figure 3.²⁰ It has D_{2h} symmetry; two La atoms are located equivalently along a C_2 axis with a long La–La distance of 3.655 Å, facing the hexagonal rings of the C_{80} cage.

It may be argued that the energetic advantage does not necessarily mean abundant production because abundance depends on growth processes and kinetics. By analyzing the ^{13}C and ^{139}La NMR spectra observed for $La_2@C_{80}$, however, we have recently verified that two La atoms are trapped equivalently inside the I_h cage.²² This again gives strong support to the view that an energetically stable structure with a large HOMO–LUMO gap is produced and isolated as a major product even for endohedral metallofullerenes, as is so for empty fullerenes. It appears that cage-like structures with metals inside (or outside) are first formed through several steps. In many cases, the initial cages do not correspond to the stable structures. However, they are able to isomerize to find stable fullerene cages during the annealing process, because the overall process is highly exothermic.

Calculations show that two La atoms in $La_2@C_{80}$ can make the circuit of the inside of the round I_h cage with small barriers of ca. 5 kcal/mol.¹³ The circuit of two La^{3+} cations produces a new magnetic field at the position of La. The interaction of La nuclear spins and the magnetic field (the so-called spin-rotation interaction)²³ significantly affects the relaxation time and thus increases the ^{139}La linewidth with an increase in

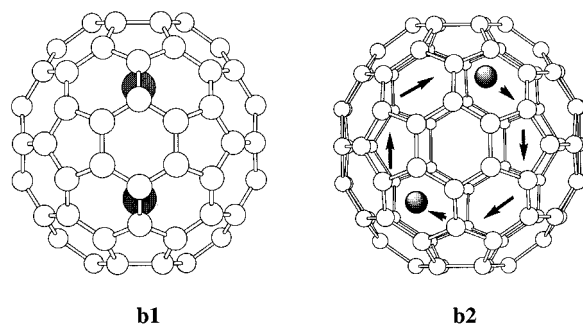


FIGURE 3. The static endohedral D_{2h} structure (**b1**) of $La_2@C_{80}$ and the dynamic structure (**b2**) with I_h symmetry due to the rapid circular motion of two La atoms.

temperature. By observing a large broadening of the linewidth with increasing temperature, we have found that the La atoms are circulating inside the round cage even at room temperature (see **b2** in Fig. 3),²² in contrast to the Sc atoms in $\text{Sc}_2@\text{C}_{84}$.^{13,15} This is the first experimental evidence of the circular motion of metals at room temperature. The small rotational barriers suggest that two La atoms can stop at the most stable positions with a decrease in temperature. Therefore, the ^{13}C NMR measurements were carried out at lower temperatures. By decreasing temperature to 258 K, broad ^{13}C NMR signals were observed which are ascribed to the overlap of ^{13}C NMR lines,²² as expected from the static D_{2h} structure (**b1** in Fig. 3) with 13 nonequivalent carbons. It is expected that the dynamic behaviors of encapsulated metals extend the research area of endohedral metallofullerenes.

The structures and electronic states of a series of $\text{M}_2@\text{C}_{80}$ ($\text{M} = \text{Sc}, \text{Y}, \text{La}, \text{Ce}, \text{Pr}, \text{Eu}, \text{Gd}, \text{Yb}, \text{and Lu}$) have been also investigated theoretically.²⁴

$\text{M}@\text{C}_{82}$ ($\text{M} = \text{Ca}, \text{Sc}, \text{Y}, \text{and La}$)

Monometallofullerenes, $\text{M}@\text{C}_n$ ($\text{M} = \text{Sc}, \text{Y}, \text{La}, \text{and lanthanides}$), are most abundantly extracted and isolated when $n = 82$ (a special "magic" number).¹⁻⁴ Because of the difficulty in preparing the single crystals, even for $\text{M}@\text{C}_{82}$, ^{13}C NMR probes are most promising at present for the determination of cage structures and symmetry, as demonstrated for $\text{Sc}_2@\text{C}_{84}$ ¹⁴ and $\text{La}_2@\text{C}_{80}$.²² However, the paramagnetic nature prevents the NMR measurements. For this reason, the structural determination of monometallofullerenes has been delayed. In this context, the recent successful isolation and purification of the $\text{Ca}@\text{C}_{82}$ isomers²⁵ are noteworthy as the first example of group 2 metal containing fullerenes for which diamagnetic properties are expected. Thus, we have undertaken the theoretical calculations of $\text{Ca}@\text{C}_{82}$ in an attempt to predict the structural aspects of $\text{M}@\text{C}_{82}$.²⁶

For the C_{82} fullerene, there are nine isomers [C_{3v} (a), C_{3v} (b), C_{2v} , C_2 (a), C_2 (b), C_2 (c), C_s (a), C_s (b), C_s (c)] which satisfy the isolated pentagon rule. Calculations have shown that the C_2 (a) isomer is most stable.^{26,27} A ^{13}C NMR study has suggested that three isomers with C_2 , C_{2v} , and C_{3v} symmetry were produced in a ratio of 8 : 1 : 1.¹⁰ However, a recent reinvestigation of the NMR lines has revealed that only one isomer with C_2 symmetry is produced while the two minor species

are ascribed to other fullerenes.²⁸ The most abundant production of the C_2 (a) isomer has been also confirmed by the calculations with temperature effects.²⁹

It has long been an open question in which isomers of C_{82} a metal atom (M) is encapsulated. It was once assumed that M was encapsulated inside the most abundant C_2 (a) isomer. As already demonstrated, however, the cage structures of metallofullerenes do not necessarily coincide with those of abundant fullerenes, because endohedral metal-doping changes not only the stability of fullerene cages but also the inner electronic states. This is due to significant electron transfer from M to fullerene cages. In this context, the relative energies of negatively charged cages are of great help as an index for predicting the most favorable fullerene cage, as shown in the structural prediction of $\text{Sc}_2@\text{C}_{84}$ ¹⁸ and $\text{La}_2@\text{C}_{80}$.²⁴ Because two valence electrons on Ca ($4s^2$) are transferred to be singlet-paired in the LUMO of C_{82} , the relative energies calculated for the C_{82}^{2-} isomers are summarized in Figure 4, together with those of C_{82} .²⁶

As Figure 4 shows, the negative charges on C_{82} have a drastic effect on the order of relative stability of the cages. The C_2 (a) cage is most stable for C_{82} . However, it is highly destabilized by accepting two electrons and becomes the second-most unstable for C_{82}^{2-} . Instead, the C_{2v} , C_s (c), C_2 (c), and C_{3v} (a) cages, which are highly unstable for C_{82} , are drastically stabilized and become most stable for C_{82}^{2-} . These four cages are close in energy for C_{82}^{2-} . This finding is remarkable because four isomers have been extracted and isolated for $\text{Ca}@\text{C}_{82}$.²⁵ It is also noteworthy that three stable isomers have been successfully isolated for

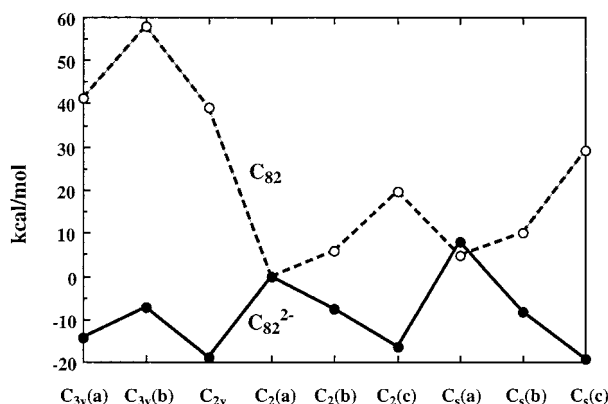


FIGURE 4. Energies of the isomers of C_{82} (a dotted line) and C_{82}^{2-} (a full line) relative to the C_2 (a) isomer.

Tm@C₈₂, which are expected to have an electronic structure of Tm²⁺@C₈₂²⁻.³⁰

The endohedral structures of Ca@C₈₂ optimized with the C_{2v}, C_s (c), C₂ (c), and C_{3v} (a) cages are denoted by **c1**–**c4** in Figure 5, respectively²⁶; for comparison, the structure (**c5**) optimized with the most stable C₂ (a) cage is also

shown in Figure 5. The optimized structures **c1**–**c5** have C_{2v}, C_s, C₂, C_{3v}, and C₂ symmetry, respectively. The Ca²⁺ cation is located at the off-center positions of C₈₂ and the favorable positions differ significantly for **c1**–**c5**. In this context, it is of interest to determine the internal nature of the C₈₂ cages. The inside of the carbon cages is originally

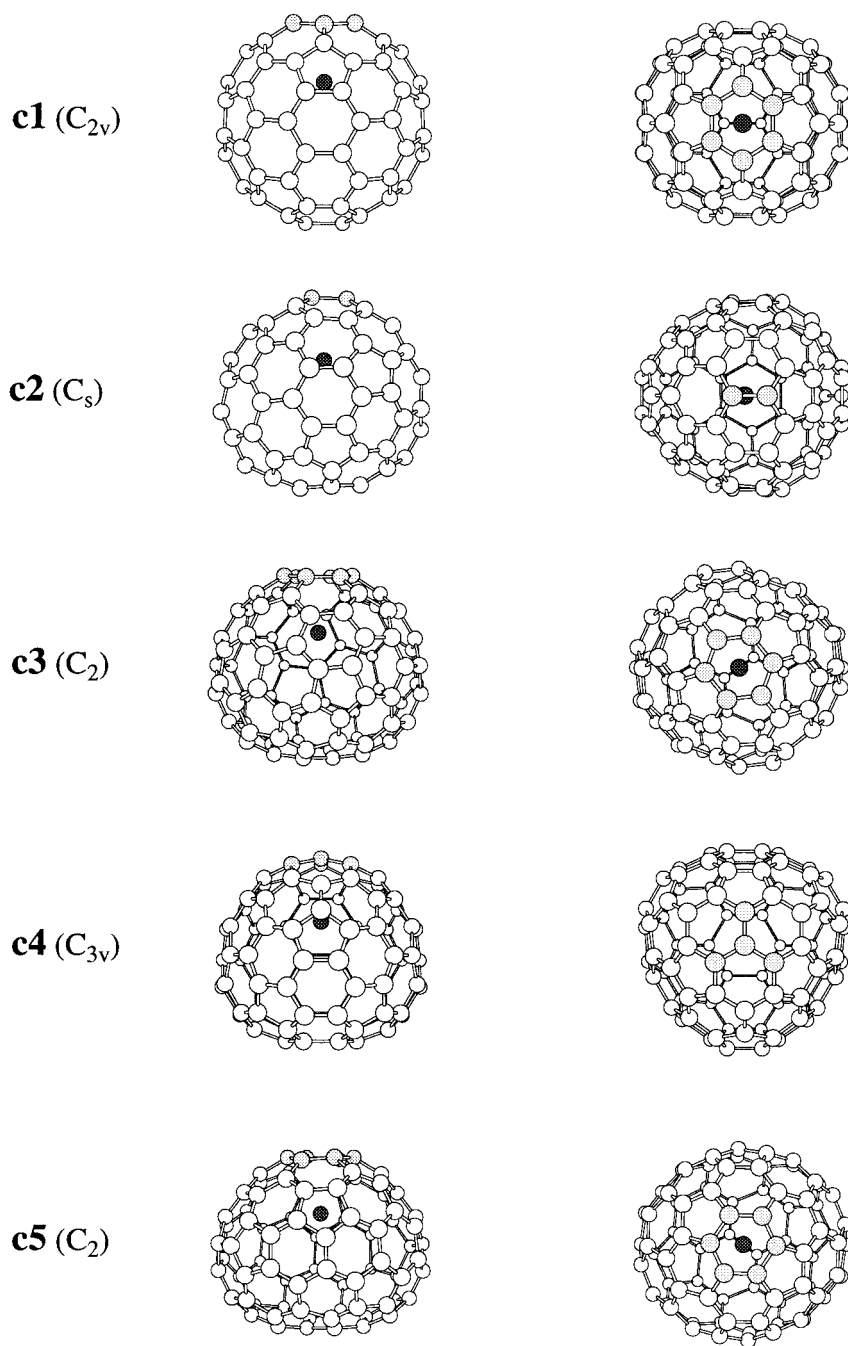


FIGURE 5. Two views of the optimized structures of the Ca@C₈₂ isomers. The distances between Ca and the nearest-neighbor carbon are 2.751 (**c1**), 2.639 (**c2**), 2.732 (**c3**), 2.629 (**c4**), and 2.738 (**c5**) Å.

suitable for accommodating anionic species, as is apparent from the fact that the electrostatic potentials inside C_{82} are positive at all positions.²⁶ Such positive values are not specific to C_{82} but rather common to neutral fullerene cages,¹³ reflecting that the probability of finding electrons inside is much smaller than that of finding them outside.

However, the situation changes drastically as electrons are transferred onto cage carbons. The inside of C_{82}^{2-} is very suitable for accommodating the Ca^{2+} cation, because the electrostatic potentials become highly negative inside the cage.²⁶ This is a reason why encapsulated metal atoms prefer cationic states. Thus, it is not surprising that the atoms entrapped up to now are those with low ionization potentials. Obviously, the Ca^{2+} cation is most highly stabilized near the minimum of the electrostatic potentials.²⁶ Consequently, the Ca atom in Figure 5 is located near the minimum. This suggests that electrostatic interactions play a dominant role both in stabilizing the endohedral structures and in determining the metal positions.

As expected from the relative energies of the C_{82}^{2-} cages in Figure 4, **c1**–**c4** are calculated to be much more stable than **c5** [encapsulation of Ca inside the most stable C_2 (a) isomer of C_{82}]; **c1** and **c2** are close in energy and most stable, whereas **c3** and **c4** are only 2–6 kcal/mol less stable than **c1** and **c2**.²⁶ Very recently, Shinohara and coworkers^{25b} have succeeded in observing a ^{13}C NMR spectrum for one of four $Ca@C_{82}$ isomers isolated under anaerobic conditions. Forty-one distinct ^{13}C NMR lines with equal intensity were observed. This agrees with structure **c3** with 41 nonequivalent carbons. It is expected that NMR probes are also successful for the remaining isomers.

It has also recently been shown that the endohedral structures optimized with the C_{2v} cage are most stable for $M@C_{82}$ ($M = Sc, Y, \text{ and } La$).³¹ As in our previous study,³² transfer of three valence electrons on M (d^1s^2) to C_{82} is increasingly favored as M changes from Sc to Y and La. $M@C_{82}$ was most highly stabilized when M approaches the center of one hexagonal ring along the C_2 axis, as structure **c1** in Figure 5 shows. This structural feature is consistent with the EXAFS studies³³ of $Y@C_{82}$ and $La@C_{82}$, which show that the number of nearest-neighbor carbons is six. The distances between M and nearest neighbor carbons are calculated to be 2.497–2.498 Å for $Sc@C_{82}$, 2.464–2.477 Å for $Y@C_{82}$, and 2.648–2.661 Å for $La@C_{82}$.³¹ It is noteworthy that the Y–C distances are in good agreement with the available

experimental values of 2.4 Å (EXAFS)^{33a} and 2.47 Å (a very recent value from the X-ray powder diffraction)^{6b} for $Y@C_{82}$. The endohedral C_{2v} structures of $M@C_{82}$ ($M = Sc, Y, \text{ and } La$) are soon expected to be verified experimentally as a major structure—because $M@C_{82}$ is a most typical metallofullerene.

Conclusions

The structural determination of endohedral metallofullerenes is progressing rapidly through a close interplay between theoretical calculations and experiments. Almost without exception, it has been found, up to now, that energetically stable structures with a large HOMO–LUMO gap are abundantly produced. It is noteworthy that the cage structures do not necessarily coincide with those of abundant fullerenes because of the important electron transfer from metals to fullerenes. Electrostatic interactions play an important role in determining the cage structures and metal positions. It is very likely that endohedral structures are formed during the annealing process.

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